

# Hydrogen production by coal plasma gasification for fuel cell technology

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## Abstract

Coal gasification in steam and air atmosphere under arc plasma conditions has been investigated with Podmoskovnyi brown coal, Kuuchekinski bituminous coal and Canadian petrocok. It was found that for those coals the gasification degree to synthesis gas were 92.3%, 95.8 and 78.6% correspondingly. The amount of produced syngas was 30–40% higher in steam than in air gasification of the coal.

The reduction of the carbon monoxide content in the hydrogen-rich reformat gas for low-temperature fuel cell applications normally involves high- and low-temperature water gas shift reactors followed by selective oxidation of residual carbon monoxide. It is shown that the carbon monoxide content can be reduced in one single reactor, which is based on an iron redox cycle. During the reduction phase of the cycle, the raw gas mixture of H<sub>2</sub> and CO reduces a Fe<sub>3</sub>O<sub>4</sub>–CeO<sub>2</sub>–ZrO<sub>2</sub> sample, while during the oxidation phase steam re-oxidizes the iron and simultaneously hydrogen is being produced. The integration of the redox iron process with a coal plasma gasification technology in future allows the production of CO<sub>x</sub>-free hydrogen.

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## 1. Introduction

Fuel cell technology has experienced a rapid development in recent years for both stationary and vehicle applications. A fuel cell transforms chemical energy directly into electrical energy and its theoretical efficiency is not limited by Carnot inefficiency problem for heat to work conversion. According to the operation temperature, fuel cells can be divided into different groups. The low-temperature fuel cells, such as proton exchange membrane (PEMFC) and alkali fuel cell (AFC) operates at temperatures from 343 to 363 K and from 343 to 473 K, respectively, and high-temperature fuel cells, such as melting carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC) operates at temperatures from 923 to 973 K and from 1073 to 1273 K, respectively [1].

These types of fuel cells utilizes hydrogen which comes from a wide range of source materials, including fossil fuels and biomass [1]. Within the next 20 years, the production amount

of oil and natural gas are expected to decrease and in the future their cost will increase continuously. Renewable energy sources will not be able to cover the total energy demand in the world: some countries will replace oil and natural gas with nuclear energy, some others with coal [2–4]. Therefore, it is important to develop coal technologies, which are clean and efficient.

Coal is the fossil fuel with the highest content of carbon and therefore it is crucial to increase the conversion efficiency. Only in that way one can reduce the carbon dioxide emissions, while waiting for effective sequestration systems. In the gasification process crushed/pulverized coal feed (either dry or as a slurry) is mixed with the oxidant (typically air or oxygen and steam) [2–9]. The coal enters into the gasifier, where it is volatilized at 1000–1500 °C and the resulting hydrocarbons react to carbon monoxide and hydrogen (syngas) according to the overall equation:



The produced syngas can be used directly as town gas, it can be used as fuel in power plant for the production of electricity,

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or it can be used for the production of synthetic fuels, e.g. methanol, Fischer–Tropsch liquid fuels.

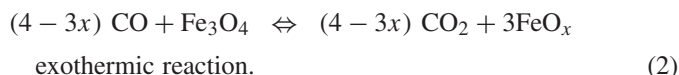
There exists currently a variety of different gasification technologies [10,11]. One of most promising one is the coal plasma gasification (CPG). The arc plasma can speed up the chemical reactions substantially and initiate some reactions which, otherwise, are difficult to carry out under normal conditions. It is well known that coal, when processed under plasma conditions, can produce hydrogen and carbon monoxide with high yield [11].

The integration of clean plasma gasification coal technology for hydrogen production to fuel cell would improve the coal conversion efficiency and provide a new route for sustainable hydrogen production.

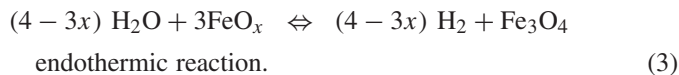
However, for PEMFC, which is the most potential fuel cell, the gasification product CO is a strong poison even when its concentration is as low as 20 ppm. The complete removal of CO to the range of some ppm by two step water gas shift reaction and by preferential oxidation is complex, bulky and expensive [1]. These drawbacks remain a serious technological obstacle in the practical utilization of these processes.

As an promising alternative to these conventional CO cleaning technologies is the iron redox cycle. This process has been developed to produce hydrogen with a quality that exceeds the requirements of all types of fuel cells and it has recently obtained an increasing attention [12–15]. This two-phase process can be performed in one single reactor without any post-processing of the gas, such as water gas shift and/or preferential oxidation. The technology is based on periodic reduction/re-oxidation cycles of iron oxides. During the first step (iron oxide reduction), gaseous hydrocarbon or syngas reduces the iron oxide to iron, Eqs. (2), (3). During the second step (iron re-oxidation), steam is used as oxidizing agent for iron, simultaneously producing hydrogen according to Eq. (4). The produced gas consists of steam and CO free hydrogen which can be directly supplied to PEMFC.

*Phase I:*



*Phase II:*



*Overall:*



This paper describes the experimental operation of plasma gasification. Pulverized solid fuels are applied as feed and the results of the experimental investigation on plasma-steam and air gasification of high ash coals and one of the most calorific solid fuel, Canadian petcoke are presented in detail.

## 2. Experimental

### 2.1. Description of the CPG laboratory-scale plant

CPG experiments were carried out on the laboratory-scale plant shown in Fig. 1. The principal components are: (i) a direct current plasma generator-reactor, 1; (ii) a synthesis gas and slag separator chamber, 2; (iii) a slag trap, 3; (iv) chamber of synthesis-gas cooling and removal, 4; (v) a pulverized coal feeding system, 7; and (vi) a steam feeding system, 13.

The zones of plasma heat release and the heat absorption by the coal and gas reactions are combined in the same plasma generator-reactor chamber, 1. It consists of a cylindrical water-cooled jacket with a top cover carrying graphite rod electrode and the inlet pipes for pulverized coal and steam. The plasma generator-reactor chamber is lined with graphite, thickness 20 mm, and bounded at its bottom side by a graphite orifice, 2. Rod electrode is cathode and ring electrode (lining of the reactor) is anode. The inner diameter of the reactor (i.e. of the graphite lining) is 150 mm and its height is 300 mm. The reactor is operated by a direct current electric power supply consisting of a transformer regulated under load and inductive choke. One electric phase is switched to the rod electrode (diameter 40 mm), with the zero phase being switched to the graphite lining. The distance between the rod electrodes and the graphite ring electrode is 55 mm. The arc is established as sketched between the rod electrode and the graphite lining electrode. It is localized at a height of 70 mm by an enveloping electromagnetic coil. Thus volume of the arc zone is about 1150 cm<sup>3</sup>. The plasmatron power can be varied between 50 and 100 kW.

The slag trap, 3, is a water-cooled cylinder of height 560 mm, containing a slag catcher basket. It is lined with graphite to give an inner diameter of 150 mm. The syngas cooling occurs in chamber 4, which is a water-cooled stainless steel cylinder, and is also lined with graphite to the same inner diameter of 150 mm.

The supply system of the pulverized coal consists of a ball mill and screw feeder, 7. The steam feeding system consists of a hot-water boiler mounted on a weighbridge, 13. The two streams are merged and partially mix prior to admission to the reactor through pipes in its top cover. The admission rate of the pulverized coal is controlled by weight within an error of 1.5%. The steam rate is varied in the range of 0–10 kg/h within an error of 3%. After the completion of an experimental run, all parts of the apparatus are thoroughly cleaned of the condensed phase, which is weighed to determine the mass of the solid residue from the coal conversion process. The yield of gaseous products is measured with an orifice plate, 5, at the outlet of synthesis-gas cooling chamber, 4.

The samples of the product gas is withdrawn directly from the reactor and from the synthesis-gas cooling chambers through a water-cooled probe and admitted to the gas analysis system. The probe is prone to clogging by particulate matter and a cleaning rod is incorporated. Samples of 50 ml are collected over periods not exceeding 10 min and gaseous samples were analyzed in a gas chromatography. The composition of the solid residue was examined by chemical and X-ray phase analyses.

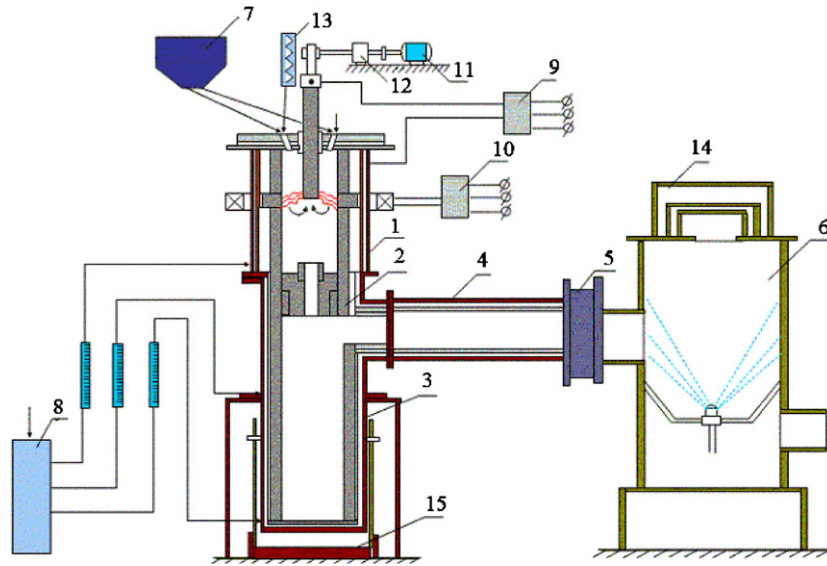


Fig. 1. Laboratory-scale plant for plasma gasification of coal: 1—DC plasma generator-reactor (gasifier); 2—gas and slag separator chamber and orifice; 3—slag trap; 4—chamber of synthesis-gas cooling and removal; 5—the system of gas flow measure; 6—chamber of hydration; 7—pulverized coal feeder; 8—the installation units cooling system; 9, 10—electric power supply system; 11, 12—motorized electrode position system; 13—water steam generator; 14—safety valve; 15—stand for slag trap.

An overall calorimetric balance was performed on the apparatus by measuring the coolant water flows and temperatures. The water temperatures are measured by thermocouples (Chromel-Copel) with an absolute error of  $0.2^\circ$ . The overall error in the calorimetric balance was typically 6–10%.

The temperatures of the reactor wall and of the gases exiting from the graphite diaphragm were measured by standard tungsten–rhodium thermocouples. The thermocouple junction exposed to the exiting gases was  $10^{-3}$  m in diameter; the radiation error did not exceed  $50^\circ\text{C}$ . The gas temperature in the reactor could not be measured. Instead, the mass-averaged temperature of reagents was calculated from a reactor heat balance.

## 2.2. Experimental procedures

The mass and heat balance is an important indicative of gasification experiments. The equations of material and heat balance of the experimental setup can be written as follows:

$$G_2 + G_3 + G_4 + G_5 = G_6 + G_1 + G_7 \text{ (kg/h)}, \quad (5)$$

$$W_0 + W_1 = W_2 + W_3 + W_4 + W_5 + W_6 \text{ (kW)}, \quad (6)$$

where  $G_2$ ,  $G_3$ ,  $G_4$ , and  $G_5$  are the flow rates of coal, plasma forming gas (steam or air), carrier gas for coal pulverization, and electrode graphite erosion, respectively;  $G_6$ ,  $G_1$ ,  $G_7$  are the mass rates of slag (solid residue), effluent gases, and fly ash (fume and fine particles) being removed, respectively;  $W_0$  is the heat output of the arc,  $W_1$  is the heat supplied with steam at  $T = 405 \text{ K}$ ; the heat losses to the cooling water in the unit assemblies are:  $W_2$  from the reactor;  $W_3$  from the gas and slag separation chamber;  $W_4$  from the synthesis-gas cooling chamber; from the slag catcher;  $W_6$  from the heat carry-over in the effluent gas stream.  $W_2$ – $W_5$  were measured using procedure

of calorimetry. Consumption of coal ( $G_2$ ) is measured using calibration graph of the coal feeder. Losses of electrode carbon ( $G_5$ ) are determined balancing electrodes before and after the experiment.

The arc heat output is determined from the electric power supplied. The heat input in steam is calculated as

$$W_1 = G_3 \cdot H_1 \text{ (kW)}, \quad (7)$$

where  $H_1 = H_{405 \text{ K}}^0 + \Delta H_{\text{steam}}^0 = 0.05 + 0.63 = 0.68 \text{ kW h/kg}$  of steam.  $\Delta H_{\text{steam}}^0$  is the heat of vaporization. The heat loss in the effluent gases is determined from the effluent gas temperature ( $T_g$ ), flow rate ( $G_1$ ), and composition obtained through the gas analysis.

The gas mixture heat output is calculated as follows:

$$W_6 = H_6 \cdot G_1 \text{ (kW)}, \quad (8)$$

where  $H_6 = \int_{300}^{T_g} C_p dT$  is the specific enthalpy of the gas mixture.

Thus, except of  $W_6$ , all the components of the heat balance equation are measured during the experiment.

A thermal coefficient for the plasma reactor ( $\xi$ ) is defined as

$$\xi = \frac{W_0 - W_2}{W_0} \cdot 100\%. \quad (9)$$

The specific power consumption,  $Q_{\text{SP}} = f(T)$  is

$$Q_{\text{SP}} = \frac{W_0 + W_1}{G_2 + G_3 + G_4 + G_5} \text{ (kW h/kg)}. \quad (10)$$

Using this value, the mass-averaged temperature of the reactor contents,  $T_{\text{AV}}$ , is determined with the help of TERRA code [16]. Reference to the preceding equation shows that, when determining  $Q_{\text{SP}}$ , only the effective power consumption of the plasma generator is taken into account.

To calculate the specific energy consumption for the process, balanced to 1 kg of gaseous products of the gasification process (syngas) output, the following formula is used:

$$Q_{SP}^{SYNG} = \frac{W_0 + W_1 - W_2}{G_1 - G_4} \text{ kWh/kg.} \quad (11)$$

The degree of coal carbon gasification  $X_C$  is determined from the carbon content of the solid residue. Specifically,  $X_C$  is calculated according to the following expression:

$$X_C = \frac{C_{bas} - C_{fin}}{C_{bas}} \cdot 100\%, \quad (12)$$

where  $C_{bas}$  is the initial amount of carbon in the coal, and  $C_{fin}$  is the final amounts of carbon in the solid residue.

### 2.3. Iron–redox process

In this study,  $\text{Fe}_3\text{O}_4\text{--CeO}_2\text{--ZrO}_2$  was investigated as iron materials for the redox process. Sample was prepared via urea hydrolysis described in detail in our early works [17]. The mixed metal salt solution was added to a 0.4 M solution of urea (99.0%, Fluka) with a salt to urea solution ratio of 2:1 (v/v). This mixture was kept at 100 °C for 24 h. After this step, the sample was allowed to cool to room temperature, then it was centrifuged in order to separate the product gel from the solution. The gel was washed with ethanol, dried overnight in an oven at 110 °C, grinded to a size of about 1  $\mu\text{m}$  and then calcinated at 850 °C for 4 h. Finally, the material was pressed, grinded and sieved. The resulting mean particle size was 0.25 mm.

Catalytic activity tests for the reduction and re-oxidation of  $\text{Fe}_3\text{O}_4\text{--CeO}_2\text{--ZrO}_2$  containing catalysts were carried out in a differential quartz tube reactor (i.d. 10 mm). Typically, 10 g of catalyst were packed between layers of quartz wool. The reactor was placed in an electric furnace equipped with K-type thermocouples. The temperature of the catalyst bed was measured by thermocouples touched to the outside and inside of the reactor at the position of the catalysts bed. The reduction of catalysts (step I of the process cycle) was performed by gas mixtures containing carbon monoxide and hydrogen, in helium. The total flow rate of the feed gas into the reactor was kept at 120 ml/min by Brooks mass flow controllers. Catalytic layers were operated in the temperature range from 700 to 825 °C.

The re-oxidation of the reduced catalysts by steam (step II of the process cycle) was performed directly after the  $\text{Fe}_3\text{O}_4\text{--CeO}_2\text{--ZrO}_2$  catalysts reduction.

The concentration of the reagents and products was monitored using an MS Agilent 5973 Network Mass Selective Detector.

The conversion degree of oxygen of the reduced material,  $X_{O_2}$ , was calculated on the basis of the amount of oxygen which theoretically could be removed from the material and the amount of oxygen which was released as gaseous products ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ):

$$X_{O_2} = \frac{N_{\text{H}_2\text{O}} + 2N_{\text{CO}_2}}{4N_{\text{Fe}_3\text{O}_4} + 0.5N_{\text{CeO}_2}} \times 100\%. \quad (13)$$

The fuel efficiency was calculated on basis of the amount of hydrogen produced during the reoxidation step (step II) and the amount of hydrogen and carbon monoxide which was used for the reduction of catalyst (step I):

$$\eta = \frac{N_{\text{H}_2^{\text{out}}}}{N_{\text{H}_2^{\text{in}}} + N_{\text{CO}^{\text{in}}}} \times 100\%. \quad (14)$$

## 3. Experimental results

### 3.1. Gasification technology

Grained coals were used in all gasification experiments. Fig. 2 shows the particle size distribution of the investigated coal after graining. The average particle size of Podmoskovnyi coal dust particles was 50  $\mu\text{m}$ . The sieve analysis of Kuuchekinski bituminous coal and Canadian petrocok particles (Fig. 2) revealed that the average particle size of the coal dust were 75 and 105  $\mu\text{m}$ , respectively.

Table 1 presents the chemical analysis of the Podmoskovnyi brown coal, Kuuchekinski bituminous coal and Canadian petrocok. Their dry basis higher calorific values are 16 130, 16 632 and 47 008 kJ/kg correspondingly.

Prior to the experiments, an estimate (using stoichiometric ratio) of the steam requirement was made, where the content of oxygen in the inorganic material of coal was ignored. Podmoskovnyi coal was investigated with the feed composition of 6.7 kg/h of coal, 2.4 kg/h of steam and 1.5 kg/h of nitrogen. The electric power applied to the reactor during an experiment was 62 kW. For experiment with Kuuchekinski coal the system was 4.0 kg/h of coal + 1.9 kg/h of steam and electric power of the reactor during the experiment was 25 kW. For experiment with Canadian petrocok the system was 2.5 kg/h of coke + 3.0 kg/h of steam and electric power of the reactor during the experiment was 60.0 kW. The specific power consumptions for the processes were found from calculations by TERRA code [10]. The difference in energy consumption for Podmoskovnyi and

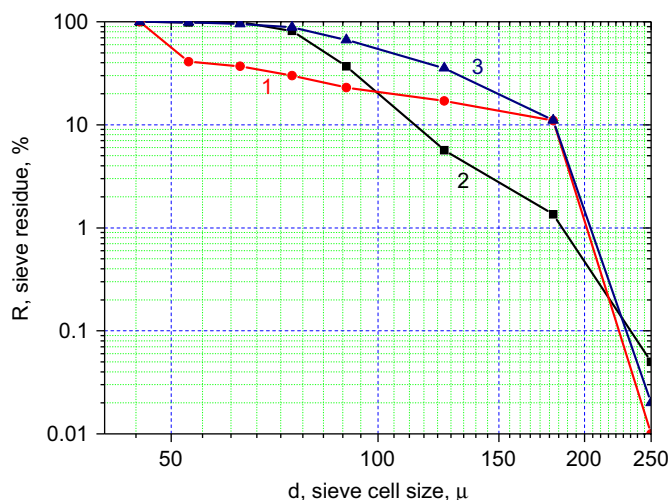


Fig. 2. Dispersed composition of the solid fuels dust: 1—Podmoskovnyi coal; 2—Kuuchekinski coal; 3—Canadian petrocok.



Table 1  
Chemical analysis of coals, mass%

| A(%)                         | C     | O    | H     | N    | S    | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | CaO  | MgO  | K <sub>2</sub> O + Na <sub>2</sub> O |
|------------------------------|-------|------|-------|------|------|------------------|--------------------------------|--------------------------------|------|------|--------------------------------------|
| Podmoskovnyi brown coal      |       |      |       |      |      |                  |                                |                                |      |      |                                      |
| 48.1                         | 33.60 | 8.52 | 6.50  | 0.88 | 2.40 | 28.52            | 16.98                          | 1.73                           | 0.41 | 0.46 | –                                    |
| Kuuchekinski bituminous coal |       |      |       |      |      |                  |                                |                                |      |      |                                      |
| 40                           | 48.86 | 6.56 | 3.05  | 0.8  | 0.73 | 23.09            | 13.8                           | 2.15                           | 0.34 | 0.31 | 0.31                                 |
| Canadian petrocokce          |       |      |       |      |      |                  |                                |                                |      |      |                                      |
| 2.95                         | 79.66 | 0.88 | 15.53 | 0.08 | 5.64 | 1.31             | 0.78                           | 0.6                            | 0.1  | 0.05 | 0.11                                 |

Table 2  
Experimental conditions of the solid fuels plasma gasification and the product gas composition

| N | G <sub>2</sub> , kg/h | G <sub>3</sub> , kg/h | G <sub>1</sub> , kg/h | Q <sub>SP</sub> <sup>SYNG</sup> , kW h/kg | T, K | Vol% |                |                |                | X <sub>C</sub> , % |
|---|-----------------------|-----------------------|-----------------------|---|------|------|----------------|----------------|----------------|--------------------|
|   |                       |                       |                       |   |      | CO   | H <sub>2</sub> | N <sub>2</sub> | O <sub>2</sub> |                    |
| 1 | 6.7                   | 2.4                   | 7.0                   | 6.1                                       | 2600 | 34.1 | 51.1           | 14.8           | 0              | 92.3               |
| 2 | 4.0                   | 1.9                   | 4.2                   | 4.8                                       | 3500 | 41.5 | 55.8           | 2.7            | 0              | 94.2               |
| 3 | 2.5                   | 3.0                   | 4.9                   | 9.8                                       | 2960 | 36.2 | 57.4           | 6.0            | 0.4            | 78.6               |
| 4 | 4.0                   | 5.1                   | 7.4                   | 3.2                                       | 2850 | 38.1 | 18.2           | 43.7           | 0              | 95.8               |

G<sub>3</sub> for experiments 1–3 is steam and G<sub>3</sub> for experiment 4 is air.

1— Podmoskovnyi coal; 2, 4—Kuuchekinski coal; 3—petrocokce.

Kuuchekinski coals is explained by significantly different consumption of the initial mixtures: 10.6 and 5.9 kg/h, respectively. As about Canadian petrocokce, it is extremely low-reaction fuel and for its gasification the increased energy consumption is required. To compare indexes (characteristics) of the gasification process depending on the influence of the oxidant type on gasification was carried out with Kuuchekinski coal. In this experiment the feed composition was 4.0 kg/h of coal and 1.9 kg/h of air, and the electric power applied to the reactor was 30 kW. The pulverized coal and steam were introduced about 15 min after initiating the arc. Steady state conditions are attained after 15 min at which time sampling began. The duration of an experiment was about 1 h.

From Table 2 one can see that the concentration of the produced hydrogen was higher than the concentration of carbon oxide in all the experiments with steam. The H<sub>2</sub>/CO ratio in the synthesis gas varied from 1.3 to 1.6. The synthesis gas yields were 85.2%, 97.3% and 92.6% for the first, second and the third experiments, respectively. For the fourth experiment, which was air gasification of Kuuchekinski coal, the H<sub>2</sub>/CO ratio in the synthesis gas was 0.5 and the synthesis gas yield 56.3%. In contrary to the investigations with Podmoskovnyi coal (experiment 1) where nitrogen was used as carrier gas, Petrocokce and Kuuchekinski coal were investigated with steam (experiments 2 and 3) or air (experiment 4) as plasma forming gas. The reader should note that 75% synthesis gas yield was obtained with the optimal parameters of plasma steam gasification of China coal from [11]. Replacing the nitrogen carrier gas by steam the concentration of synthesis gas was further increased. Solid fuel gasification degree varied from 78.6% to 95.8%. In the reported study specific power consumptions for the yield of

synthesis gas varied in a broad interval from 3.2 to 9.8 kW h/kg. Specific power consumption can be easily related to 1 kg of hydrogen. For example (experiment 2) synthesis gas consists of 8.3 mass% of H<sub>2</sub>, 84.5% of CO and 7.2% of N<sub>2</sub>. Thus specific power consumption related to 1 kg of H<sub>2</sub> will be 57.6 kW h/kg or 415 kJ/mol. As one can see in Table 2 there is no CO<sub>2</sub> in the products because at plasma gasification endothermic effect of the gasification reaction ( $C + H_2O = CO + H_2$ ) is compensated by energy from electric arc inside the gasifier. This is the principle difference from traditional processes of coal gasification in the products of which there is substantial level of CO<sub>2</sub> due to reaction of carbon combustion ( $C + O_2 = CO_2$ ). In that case this reaction compensates endothermic effect of the gasification reaction. Thermodynamic calculation of plasma steam gasification shows concentration of water steam in the products of gasification has to be about 1–2 vol%. But during gas sampling this water steam was condensing in cool sampler and it is not shown in Table 2. Cyanides (CN) in the gasification products were not measured but thermodynamic calculations for the experiments 1 and 4 (air gasification of coal) from Table 2 showed that concentration of CN cannot be more than 0.01 and 0.03 vol% for the experiments 1 and 4, respectively. Note that thermal efficiency of the plasma reactor determined by Eq. (9) was about 76% for all experiments.

The carbon monoxide and hydrogen concentrations depended on the ratio of coal and oxidant, as seen in Fig. 3. The solid lines are the thermodynamic equilibrium values which were calculated with the software package TERRA [16]. This software was developed for the simulation of high-temperature processes, especially for coal plasma processing. The thermochemical properties for more than 3500 chemical agents over a

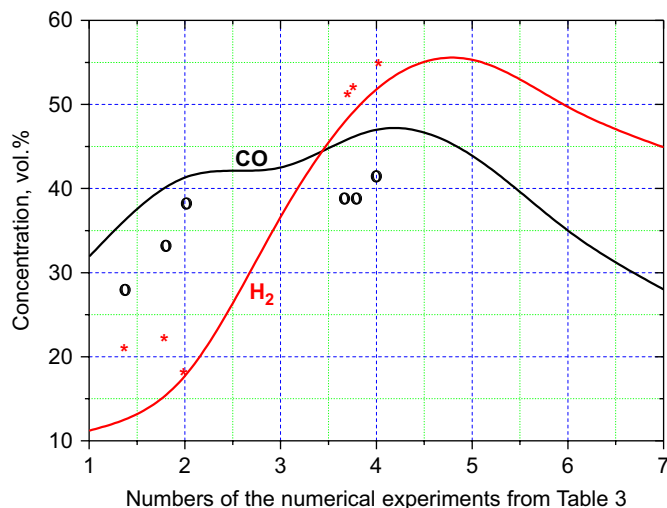


Fig. 3. Carbon monoxide (CO) and hydrogen (H<sub>2</sub>) concentration in dependence on initial conditions of experiments on Kuuchekinski coal air and steam gasification. Line is calculation by TERRA code; ° is experimental values of CO; \* is experimental values of H<sub>2</sub>.

Table 3  
Initial conditions of numerical experiments on Kuuchekinski coal air and steam gasification

| Number of variant | G <sub>2</sub> , kg/h | G <sub>3</sub> , kg/h |        |
|-------------------|-----------------------|-----------------------|--------|
|                   |                       | Air                   | Steam  |
| 1                 | 100                   | 255.0                 | –      |
| 2                 | 100                   | 127.5                 | –      |
| 3                 | 100                   | 63.75                 | 31.38  |
| 4                 | 100                   | –                     | 47.5   |
| 5                 | 100                   | –                     | 62.75  |
| 6                 | 100                   | –                     | 94.125 |
| 7                 | 100                   | –                     | 125.5  |

temperature range of 300–6000 K are included in the software package. The thermodynamic calculations for Kuuchekinski bituminous coal (Table 1) for the temperature range from 400 to 4000 K at pressure 0.1 MPa was performed. Numerals in abscissa axis correspond to the used for the calculations variants from Table 3. The difference of the variants consists in coal–oxidant ratio in initial thermodynamic system (initial mixture of coal and oxidant). Numerals “1”–“7” in the axis correspond to the initial mixtures of coal and oxidant consisted of air and water steam as represented in Table 3. As Fig. 3 clearly shows, CO and H<sub>2</sub> concentrations calculated with the model agreed qualitatively the experimental data. The concentration of hydrogen and carbon monoxide strongly depends on the initial ratio of coal and oxygen/steam. It was found that degree of coal carbon gasification,  $X_C$ , can be as high as 95.8%, whereas the H<sub>2</sub> + CO content was as high as 97.4 vol%. During the gasification of coal the concentration of synthesis gas was approximately 30–40% higher with steam than that with air.

Technical and economical justification of effectiveness of plasma coal gasification technology by the example of synthesis gas producing from Kuuchekinski bituminous coal was

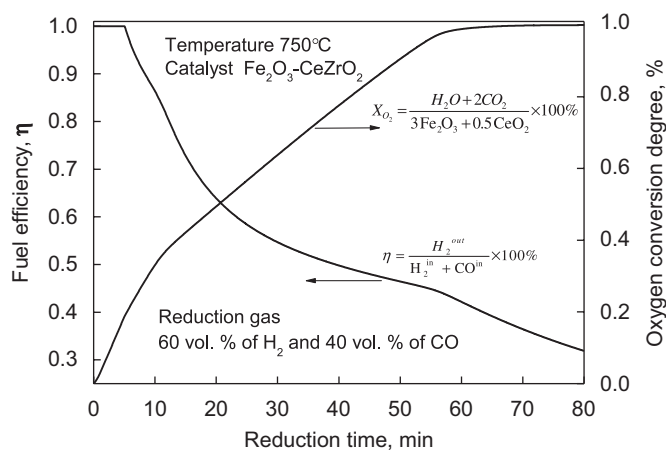


Fig. 4. The fuel efficiency calculated by the ratio of values of generated hydrogen and input reduction gas and a degree of oxygen conversion as a function of reduction time.

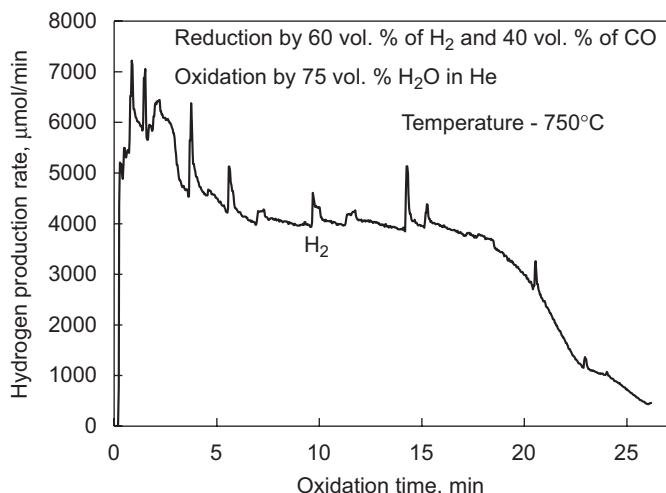


Fig. 5. Formation rates of H<sub>2</sub> during the re-oxidation phase with H<sub>2</sub>O/He for Fe<sub>3</sub>O<sub>4</sub>–CeO<sub>2</sub>–ZrO<sub>2</sub> catalyst samples after initial catalyst reduction using H<sub>2</sub> and CO. (Reaction conditions are given in the legend.)

fulfilled. The cost of synthesis gas produced at the laboratory setup (189 \$ per ton) is 8.6% lower than its market price. The cost of synthesis gas produced at the industrial plasma plant (119 \$ per ton) will be 42.5% lower than its market price. These figures show economic efficiency of plasma technology of synthesis gas production from cheap low-rank coals as compared with traditional technology of synthesis gas production through catalytic steam conversion of expensive and deficient natural gas which cost goes up to 350 \$ per ton.

### 3.2. CO<sub>x</sub> cleaning hydrogen by iron–redox process

In the present study it was not possible to combine the CPG with iron redox cycle reactor. However, in order to consider the potentiality of combining these two processes in the future, we investigated here the unit processes separately. The iron oxide process was investigated with a simulated gas mixture

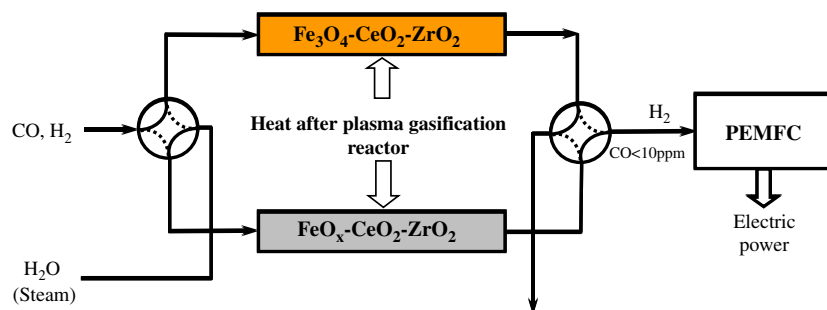


Fig. 6. Schematic diagram of a fuel processing system in a periodically operated reactor for a PEM fuel cell.

corresponding to gas product stream with the CPG. The gas mixture was conducted over the iron oxide and the syngas (60 vol% of  $H_2$  and 40 vol% of CO) reduced the iron oxide according to Eqs. (1) and (2). The efficiency of oxygen storage materials can be defined in terms of activity and lifetime. The main challenge for the realization of iron redox cycles technology is the fast deactivation of iron oxide due to a strong sintering of the material. The ability of the oxygen storage material to remain its high activity in repeated reduction/oxidation is the main factor which controls the economic viability of iron–redox process. The first experiment showed us that iron oxides owing high surface area are deactivated fastly due to the material sintering. We have seen in our prior studies that the addition of  $CeO_2-ZrO_2$  to the iron oxide mitigated the fast sintering of the iron material during the redox cycles. Furthermore,  $Fe_3O_4-CeO_2-ZrO_2$  significantly increased both the rate of syngas conversion (sample reduction) as well as the sample oxidation by water compared to pure  $Fe_3O_4$  [13,17].

The catalysts reduce reaction carry out before an oxygen conversion degree in sample was not high than 60%. We have seen in our early work [17] that low oxygen conversion degree protected catalyst from carbon deposition, which was possibly produced by the Boudouard reaction. Moreover, as shown in Fig. 4, high efficiency of the process could be achieved at low oxygen conversion level in the sample. High oxygen conversion increases the amount of not converted syngas. Fuel efficiency of cyclic reactor was 60% at the reaction temperature 750 °C.

By addition of steam into the reactor, pure hydrogen was produced and reduced iron and ceria oxides were re-oxidized for the next redox cycle. Fig. 5 shows the hydrogen formation rate as a function of time during the oxidation with water vapor of  $Fe-CeO_2-ZrO_2$  sample at 750 °C. Long-term stability of catalyst is crucial for the economic feasibility of the whole process. We were able to repeat the redox cycles 100 times. Deactivation of catalyst was lower than 20%. The surface area decreased from 15 m<sup>2</sup>/g to value 11 m<sup>2</sup>/g. This indicates that sintering is occurring during the repeated redox cycles.

Hydrogen can be used in PEMFC if the CO content is below 30 ppm. Cyclic iron redox reactor produced hydrogen sufficiently pure than used in any kind of fuel cell ( $CO < 15-20$  ppm,  $CO_2 < 20$  ppm).

For production of hydrogen continuous we will assemble several iron–redox cycle reactors working at different stage as

shown in Fig. 6. We established the number of redox reactors as follows: one/two reactors for the reduction, and one/two reactor for oxidation. All reactor have the same temperature. The heat will be supplied by heat recovery with plasma gasification reactor. At initial time redox reactor I starts with the reduction. When reduction of I reactor completed water vapor feed to this reactor for hydrogen production. After reduction of I reactor, reactor II starts with reduction. After some time one redox cycle for reactor I is completed. Then this reactor starts again with the reduction step.

These results indicated that it is possible integrate the redox iron process with a CPG technology should allows the production of CO-free hydrogen without syngas intermediate. The development of this process is in progress though a scale up route, reforming control, fluid dynamic and economical criteria.

#### 4. Conclusions

Coal gasification in steam and air atmosphere under arc plasma conditions has been tested with Podmoskovnyi brown coal, Kuuchekinski bituminous coal and Canadian petrocok. It has been found that degree of coal carbon gasification  $X_C$  to synthesis gas were 92.3%, 95.8 and 78.6% correspondingly. During the gasification of coal at steam the concentration of synthesis gas was on 30–40% higher than during at coal gasification in air.

The aim of the forthcoming investigations is optimization of the gasification process, producing of synthesis gas with specified ratio  $H_2/CO$  and decrease of specific power consumptions for the process. We see the possibility of this decrease by exit gas heat utilization for water steam production, as well as increasing of reagents consumption and using of exit gas as carrier gas for coal.

It was shown that the carbon monoxide content can be reduced in one single reactor, which is based on an iron redox cyclic process. During the reduction phase of the cycle, the raw gas mixture of  $H_2$  and CO reduces a  $Fe_3O_4-CeO_2-ZrO_2$  sample, while during the oxidation phase steam re-oxidizes the iron and simultaneously  $CO_x$ -free hydrogen is being produced.

Combining these technologies has been recognized as a suitable option for efficient stationary power generation. Also, the simultaneous production of power and useful heat from a single plant, i.e. cogeneration or combined heat and power plant,

is a very useful option for improving the overall performance of the energy conversion system.

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